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CONDUCTANCES OF STRONG SOLUTIONS OF STRONG ELECTROLYTES¹

By ALAN N. CAMPBELL AND ELINOR M. KARTZMARK²

Abstract

The conductances, densities, and viscosities of solutions of silver nitrate and of ammonium nitrate, at 25°C., have been determined at concentrations ranging from 0.1 *N* to saturation (about 9 and 11 *N* respectively). By way of comparison, the same data have been obtained for the weak electrolyte acetic acid, up to 99.7% by weight concentration. It is shown that the weak electrolyte, at these concentrations, deviates even more from the Ostwald dilution law than do the strong electrolytes. Various attempts have been made to correct the conductance for viscosity. In addition to the older methods, two new attempts have been made, viz.; sugar was added to *N*/10 silver nitrate (used as the basis for these calculations) until its viscosity became equal to each of the silver nitrate solutions in turn. The conductance of a *N*/10 silver nitrate solution containing enough sugar to make its viscosity exactly equal to that of any given silver nitrate solution was used in the evaluation of the conductance ratio. Again, the viscosities of silver nitrate solutions at different temperatures were determined and the conductance found at the temperature at which the viscosity had become equal to that of *N*/10 silver nitrate at 25°C. This conductance was used as the numerator in the conductance ratio. All attempts, however, resulted in "over-correction", that is, in an apparently increasing equivalent conductance, with increasing concentration, after a certain concentration is reached. It is shown that a remarkable agreement exists, in the case of ammonium nitrate, with the Walden modification of the Ostwald formula.

It is supposed by the casual student that what used to be called the "Anomaly of Strong Electrolytes" has been disposed of by the introduction of the theories of Debye and Hückel, Onsager, Shedlovsky *et al.*, and that the behavior of strong electrolytes is now accounted for in a completely satisfactory manner. The special student of this subject is aware that for concentrations greater than 0.01 *N*, or at most 0.1 *N* (cf. Shedlovsky (26)), the situation is as unsatisfactory as ever. It is only necessary to apply any of the equations governing the conductances of weak solutions to solutions of the same substances at high concentrations, and to compare these calculated conductances with such experimental results as are available, to realize that the disagreement with modern theories, or rather accepted equations, is greater than that with the old Ostwald dilution law. It is, too, in the range of concentration greater than 0.1 *N* that the equivalent conductance changes most, the equivalent conductance at 0.1 *N* being about 85% of its limiting value.

This is not to say that the assumptions of the modern theories are not applicable to concentrated solutions, but it is obvious that in addition to these many other factors are involved, such as viscosity, either of solvent or solution, change of degree of hydration of ions, change of dielectric constant of the

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medium, possible union of ions to form neutral molecules or ion-pairs (1). An excellent discussion of the effect on conductance (in concentrated solution) of these and other factors is given by Ritson and Hasted in a recent paper (22).

The X-ray study of crystal structure led to the accepted view that ionization of a salt is already complete in the lattice and that, therefore, it would be illogical to suppose that when the lattice is broken up by the action of a solvent, union to neutral molecules takes place, followed by subsequent dissociation to complete ionization at high dilution. This opinion no doubt aided in the overthrow of the Arrhenius conception of partial ionization. Looked at more closely, however, there seems nothing illogical in the view that after the ions are given freedom of movement by the break-up of the lattice, some of them should unite to form what, for lack of a better term, may be called neutral molecules. That electrolytes can form neutral molecules is obvious from the behavior of hydrogen chloride gas and other volatile electrolytes, whose vapor densities are normal. The neutral molecules in solution, if such exist, may be of a different, less stable type, as postulated by Bjerrum, but if any such association of ions, however loose, is electrically neutral as a whole, it ceases to be a conductor of electricity and this would cause the equivalent conductance to decrease with increasing concentration, essentially after the manner required by Arrhenius. No doubt, other factors contribute to the decrease in conductance as well; indeed, there is no *a priori* reason to believe in the existence of neutral molecules in solution, although von Halban (9) and Fajans (5) claim to have demonstrated, by light absorption experiments, their existence in concentrated solutions. If an equilibrium between ions and neutral molecules really exists in electrolytic solutions the Ostwald dilution law, or some similar formula, must be applicable, provided the true value of α , the degree of dissociation, can be obtained. It is obvious that under no circumstances does the simple conductance ratio measure the degree of dissociation. It is pointed out by Glasstone (7) that, on the assumption of two oppositely charged ions, the following relation must apply:

$$\alpha = \frac{\Lambda}{\Lambda_0} \cdot \frac{\mu_+^0 + \mu_-^0}{\mu_+ + \mu_-}.$$

The old classical theory assumed that $\frac{\mu_+^0 + \mu_-^0}{\mu_+ + \mu_-}$ was always equal to unity,

independent of concentration, and that, therefore, $\alpha = \frac{\Lambda}{\Lambda_0}$. The modern theory

assumes $\alpha = 1$, and therefore $\frac{\Lambda}{\Lambda_0} = \frac{\mu_+ + \mu_-}{\mu_+^0 + \mu_-^0}$. It is possible that, in con-

centrated solutions, the truth lies somewhere between the two views. The success of the Debye-Hückel-Onsager theory shows that, at least in dilute solutions, the ionization is complete. We are not without hope that, at a future date, we may be able to determine the ratio of ion velocities at different (high) concentrations and thus settle the question of partial or complete ionization.

The older literature abounds with efforts to incorporate a viscosity correction in the determination of α from conductance ratio. It is pointed out by Sachanov (24, 25) and Rabinovich (21) that merely to multiply the conductance ratio by η , the ratio of the fluidity of water to that of the solution, leads eventually to "overcorrection", i.e., to an apparently increasing α with increasing concentration. Dilution law "constants", calculated with this corrected value of α , increase enormously with concentration. It seems evident to us that the external viscosity of a solution, measured in an ordinary viscometer, does not represent the true resistance to the movement of the ions, but we are not aware of any experimental method whereby the true, internal viscosity may be determined.

Walden (28) thinks that, in the dilution law formula, and also in the calculation of equivalent conductance, the dilution should be represented, not by the volume of solution containing an equivalent, but by the volume of water in the solution, $\phi - \phi'$, where ϕ' is the equivalent volume of the electrolyte in the anhydrous condition. Since, however, on this assumption $\Lambda = L(\phi - \phi')$, the Ostwald dilution formula assumes the shape

$$k = \frac{L^2(\phi - \phi')}{\Lambda_0^2 \left(1 - \frac{L(\phi - \phi')}{\Lambda_0}\right)},$$

(where L is the specific conductance). The value of k must necessarily reduce to zero for the anhydrous electrolyte, since $\phi - \phi' = 0$, and indeed our own observation on 99.7% acetic acid shows this. Despite this obvious objection, we have used the Walden formula, among others, to express our results, and there is a noticeable approach to constancy in the case of ammonium nitrate. Our range is of course limited by the solubility at 25°C., which amounts to 9 to 10 molar.

The aim of the present work is to obtain accurate figures for the conductances of two typical (binary) strong electrolytes over the complete range of concentration from 0.1 N to the anhydrous condition. This entails determinations at temperatures above the melting point and in sealed vessels. The main object of the investigation is to discover how the equivalent conductance changes from the breakdown of the (completely ionized) lattice down to comparatively dilute solutions. As substances with readily accessible melting points we chose silver nitrate (m.p. 218°C.) and ammonium nitrate (m.p. 169°C.); the complete solubility diagrams of these salts, up to their melting points, are known (2, 17).

As a preliminary to the more difficult work we thought it advisable to carry the investigation as far as possible at 25°C. and this, our first paper, contains the results for that temperature. As the basis of reference for our conductance ratios and relative viscosities we chose, not limiting conductance and viscosity of water, but the conductance and viscosity of $N/10$ solutions. The reason for this is the fact that the modern theories of complete ionization account satisfactorily for the behavior of electrolytic solutions up to this concentration, and

therefore any decrease in conductance due to partial ionization must occur at concentrations higher than this. Since, however, the extension of Onsager's equation by Shedlovsky is purely empirical, the 0.01 *N* solution might have been a better basis of reference.

This paper contains, in addition to the conductance data, the relevant data on density and viscosity that were obtained as a part of these determinations.

In our endeavors to apply a viscosity correction, we developed two other procedures which, though not successful for the purpose for which they were devised, are instructive. Taking the *N*/10 concentration as our standard of reference, we added successive amounts of cane sugar to *N*/10 silver nitrate and determined the density and viscosity. Plotting the viscosity against the sugar content, we were able to interpolate the sugar content corresponding to the viscosity of silver nitrate of any desired normality. A solution, decinormal with respect to silver nitrate and containing the requisite amount of sugar, was then made up and its equivalent conductance determined. This conductance was then used as the denominator in the quotient $\frac{\Lambda_c}{\Lambda_{0.1 + \text{sugar}}}$, instead of, as usual, multiplying the conductance ratio by the relative fluidity.

In a second attempt to compare the conductances of solutions at different concentrations, we abandoned the isothermal approach and determined the viscosities of a given solution at a series of temperatures from 25°C. upwards. We were thus able to interpolate a temperature at which the viscosity of a given solution was the same as that of *N*/10 silver nitrate at 25°C. The conductance of the solution at this temperature was then determined and the quotient $\frac{\Lambda_p}{\Lambda_{0.1N \text{ at } 25^\circ}}$ evaluated. The results of these calculations and a dis-

cussion of their significance are given later, but we reserve for another paper the significance of these figures as to the effect of temperature on viscosity and conductance of strong solutions.

Since it is frequently stated that weak electrolytes obey (approximately) the Ostwald dilution law, we have also determined the equivalent conductance of acetic acid up to a concentration of 99.7% by weight.

Further work will be concerned with a repetition of the conductances at 95°C., and at temperatures above the respective melting points.

Existing Literature

A bibliography of existing literature is given at the end. (Nos. 6, 8, 10, 11, 13, 14, 15, 16, 18, 19, 20, 21, 23, 24, 25, 26, 27, 28, 29.)

To summarize: (1) Few determinations of the conductances of concentrated solutions of strong electrolytes have been made, and none at the very highest concentrations; (2) such determinations as exist were all made by the old Kohlrausch technique, although it must be admitted that modern refinements are not so necessary for these highly conducting solutions; (3) all theoretical

speculators are convinced of the necessity for a viscosity correction, although most are aware that the viscosity correction as usually applied, that is, the simple multiplication by the ratio of the viscosity to that of water, leads to "overcorrection", i.e., to an apparently increasing equivalent conductance, with increasing concentration. Such an increasing conductance could not be explained on the old basis of partial ionization nor, presumably, on that of modern theories. In the absence of experimental data, though unpossessed ourselves of any constructive theory in this difficult subject, we felt ourselves justified in proceeding with the experimental work described in this paper.

Experimental Techniques

The precautions and refinements to be observed in modern work on conductance are scattered through the literature in papers by Jones, Scatchard *et al.* and their collaborators. Most of it is to be found in any good modern textbook, such as that of Davies (4). While adhering scrupulously to most of the conditions laid down, we did not find it necessary to use the very highest accuracy in the determination of conductance, such, for example, as that involved in the use of the Jones conductance bridge, because the multiplying factor of dilution was relatively small. For the same reason, the correction for conductance of pure solvent was quite negligible, except in our work on acetic acid, and it was therefore sufficient for us to use a good distilled water in place of conductance water. Again, the electrical capacity of these solutions is almost negligible.

Purity of Materials

Silver nitrate was obtained from the Johnson, Matthey, and Mallock Company. The analysis supplied showed it to be very pure, with the exception of a trace of moisture. It was not recrystallized but was kept over sulphuric acid in a desiccator. The ammonium nitrate was part of a large consignment from the Consolidated Mining and Smelting Company, of Trail, B.C., which was supplied during the war years. Although it was a commercial product, the analysis supplied at the time of delivery showed it to be very pure. Nevertheless, it was recrystallized from water and dried, first on porous plates and then over sulphuric acid for a month.

Solutions were all made up by weighing, as were all aliquot portions, so as to be independent of graduated apparatus. The water used in making solutions was a good quality distilled water, having $L = 5.28 \times 10^{-6}$ mho. With these highly conducting solutions there is no necessity for using highly purified conductivity water. The dilutions were arrived at by weighing the solutions and determining the densities. Merck glacial acetic acid was used in the preparation of the acetic acid solutions and all these solutions were analyzed with standard sodium hydroxide.

Conductance Measurements

The apparatus used was an exact duplicate of that given on page 17 of the Leeds and Northrup catalogue, "Electrolytic Conductivity Measurements", (1944), except that the audio-frequency amplifier was found unnecessary for

these highly conducting solutions; a simple telephone headpiece was used as detector. The instruments themselves were obtained from the Leeds and Northrup Company (e.g., the standard resistance box), so that the accuracy is that claimed by that firm. Variation in frequency had no effect on the results and the capacity correction ($R_s = R_p \cos^2 \alpha$) was quite negligible. The usual frequency used was $\omega = 1000$. Four different conductivity cells were used, whose resistances (when filled with appropriate solutions) and electrode areas were such as to comply with the Kohlrausch rule

$$R_c = K/Q \quad (K > 100).$$

All cells were of the type recommended by Jones and Bollinger (12) for highly conducting solutions. The respective cell constants were 33.64, 38.42, 148.94, and 209.76, and the resistances of different solutions varied from 200 to 1200 ohms. At least two cells were used for each determination. Apart from occasional variation, the specific conductances were identical, within the limit of error, whatever cell was used. End points on the bridge were absolutely silent and sharp. The only detectable variation in bridge setting was obviously caused by the fluctuation of our thermostat, viz., $\pm 0.01^\circ\text{C}$. Allowing the usual 2% per degree temperature variation of conductance, this temperature fluctuation produces an uncertainty of 0.02% in our results. The accuracy of the apparatus is 0.1% and our over-all error is no greater. Where published figures are available they do not differ from ours by more than, at most, one unit, but this difference is much greater than our error. We therefore believe that such differences are real and to be attributed to the fact that the earlier workers used the simple Kohlrausch bridge, without refinements. The Campbell-Shackleton bridge used by us eliminates many of the unavoidable errors of the historical apparatus. The temperature of the thermostat was $24.99 \pm 0.01^\circ\text{C}$.

To obviate errors due to capacity effect we used paraffin oil as thermostatic liquid (Davies (4, p. 40)). Connection of the cell to the circuit was made via two large mercury wells and all connecting wires were heavily insulated, rigid, and far from one another so that errors of poor insulation and induction effects were avoided. Wires were shielded and the circuit grounded as recommended by Leeds and Northrup. Cell constants were determined using 0.1 *N* and 1.0 *N* potassium chloride and, for acetic acid, 0.01 *N* potassium chloride. The potassium chloride used was of the highest purity but it was recrystallized by us, ignited, and kept over sulphuric acid.

We have found by experience that the principal error of our work lies neither in the determination of conductance nor that of density, but in the weighing of the 100-ml. flasks containing the solutions, which had to be done on a relatively coarse balance.

Density Measurements

These were made in a Weld pycnometer of about 25 ml. capacity, using the precautions and experience gained in previous work (3). While, however, Campbell and Miller found it necessary to obtain an accuracy of at least ± 0.0001 in their density measurements, in this somewhat more rapid work we are content to claim an accuracy of 0.001, which is fully sufficient.

Viscosity

These determinations were made in the usual way, using an Ostwald viscosimeter calibrated with water.

Numerical Results

Some of the experimental results are given in Table I, which contains the specific and equivalent conductances, densities, and viscosities, at 24.99°C.

TABLE I
SPECIFIC AND EQUIVALENT CONDUCTANCES, DENSITIES, AND VISCOSITIES, OF SILVER NITRATE
AND OF AMMONIUM NITRATE, AT 24.99°C.

Concentration		Spec. cond., mhos	Equiv. cond., Λ	Density, gm./ml.	Relative viscosity	
Wt. %	Molarity				A	B
A. Silver nitrate						
1.68	0.100	0.01091	109.1	1.011	1.009	1.000
15.01	1.004	0.07815	77.82	1.137	1.074	1.065
26.74	1.998	0.1303	64.20	1.276	1.177	1.167
36.41	3.028	0.1665	54.97	1.413	1.307	1.295
44.02	4.000	0.1940	48.50	1.544	1.472	1.459
50.71	5.029	0.2168	43.14	1.685	1.658	1.643
59.28	6.006	0.2316	38.55	1.810	1.890	1.873
61.30	7.012	0.2413	34.70	1.943	2.170	2.151
65.61	8.011	0.2501	31.20	2.075	2.505	2.483
69.45	9.010	0.2522	27.99	2.203	2.998	2.971
71.59	9.709	0.2523	26.1	2.298	3.330	3.303
B. Ammonium nitrate						
0.80	0.100	0.01227	112.95	1.001	0.991	1.000
7.81	1.004	0.1017	101.32	1.029	0.960	0.969
15.06	1.993	0.1833	91.95	1.059	0.952	0.960
21.91	2.982	0.2513	84.28	1.089	0.977	0.986
28.74	4.020	0.3085	76.78	1.120	1.009	1.018
34.93	5.014	0.3507	70.00	1.149	1.061	1.070
41.01	6.036	0.3809	63.12	1.178	1.144	1.154
46.54	7.015	0.3979	56.73	1.206	1.234	1.245
51.98	8.011	0.4036	50.36	1.234	1.366	1.379
57.31	9.043	0.3973	43.93	1.262	1.531	1.535
62.14	10.004	0.3819	38.19	1.289	1.776	1.792
68.49	11.282	0.3538	31.3	1.319	2.170	2.190
C. Acetic acid						
10.30	1.735	1.74×10^{-3}	1.003	1.011	1.197	
20.19	3.437	1.83×10^{-3}	5.31×10^{-1}	1.024	1.407
30.15	5.206	1.61×10^{-3}	3.09×10^{-1}	1.036	1.640
38.79	6.751	1.31×10^{-3}	1.94×10^{-1}	1.044	1.833
48.04	8.423	9.47×10^{-4}	1.12×10^{-1}	1.052	2.038
57.32	10.106	6.14×10^{-4}	6.08×10^{-2}	1.058	2.259
67.10	11.883	3.33×10^{-4}	2.80×10^{-2}	1.063	2.473
76.52	13.585	1.32×10^{-4}	1.79×10^{-3}	1.065	2.635
87.09	15.415	2.30×10^{-5}	3.55×10^{-4}	1.062	2.449
99.76	17.360	$2.30 \times 10^{-7*}$	3.99×10^{-6}	1.044	1.268

*Not corrected for conductance of water.

TABLE II
DEGREE OF DISSOCIATION AND "EQUILIBRIUM CONSTANTS", ON VARIOUS ASSUMPTIONS,
OF SILVER NITRATE, AMONIUM NITRATE, AND ACETIC ACID, AT 25°C.

Concen- tration, moles per liter	Equiv. cond., Λ	$\alpha_1 = \frac{\Lambda}{N/10}$	$\alpha_2 = \frac{\Lambda}{N/10} \times \eta$	$\alpha_3 = \frac{\Lambda}{N/10} \times \eta$	$\alpha_4 = \frac{\Lambda}{N/10} \times \eta$	$K_1 = \frac{\alpha_1^2 c}{1 - \alpha_1}$	$K_2 = \frac{\alpha_2^2 c}{1 - \alpha_2}$	$K_3 = \frac{\alpha_3^2}{(1 - \alpha_3)(\phi - \phi')}$
<i>A. Silver nitrate</i>								
1.0	77.82	0.714	0.760	74.7	0.729	1.783	2.407	2.054
2.0	64.20	0.588	0.688	59.0	0.631	1.678	3.034	2.347
3.0	54.97	0.504	0.653	48.2	0.572	1.536	3.687	2.642
4.0	48.50	0.445	0.649	40.6	0.543	1.428	4.800	3.085
5.0	43.14	0.395	0.650	34.3	0.516	1.290	6.035	3.481
6.0	38.55	0.353	0.662	29.1	0.478	1.158	6.485	3.492
7.0	34.70	0.318	0.684	24.7	0.488	1.036	8.892	3.262
8.0	31.20	0.286	0.710	21.0	0.478	0.936	13.904	3.290
9.0	27.99	0.257	0.762	17.7	0.482	0.801	21.960	6.397
9.709	26.1	0.239	0.790	13.1	0.475	0.729	28.86	6.921

(This table is concluded below, on page 51)

TABLE II (Concluded)

B. Ammonium nitrate								
1.0	101.32	0.823	0.708	96.6	0.764	3.827	3.153	2.590
2.0	91.95	0.748	0.718	83.5	0.652	4.440	3.656	2.684
3.0	84.28	0.685	0.706	72.7	0.582	4.473	4.085	2.805
4.0	76.78	0.624	0.635	62.5	0.517	4.144	4.420	2.734
5.0	70.00	0.569	0.609	53.7	0.468	3.755	4.742	2.689
6.0	63.12	0.513	0.592	45.4	0.427	3.242	5.172	2.607
7.0	56.73	0.461	0.573	38.3	0.388	2.760	5.383	2.557
8.0	50.36	0.410	0.565	31.6	0.355	2.280	5.882	2.492
9.0	43.93	0.357	0.548	25.5	0.318	1.782	5.976	2.310
10.0	38.19	0.310	0.556	20.4	0.298	1.393	6.963	2.365
11.282	31.3	0.255	0.557	14.9	0.265	0.983	7.894	2.264

C. Acetic acid								
1.735	1.003	2.58×10^{-3}	3.09×10^{-3}	9.03×10^{-4}	2.78×10^{-3}	1.15×10^{-3}	1.65×10^{-6}	1.49×10^{-4}
3.437	5.31×10^{-1}	1.37×10^{-3}	1.92×10^{-3}	4.27×10^{-4}	1.54×10^{-3}	6.42×10^{-4}	1.27×10^{-6}	1.02×10^{-4}
5.206	3.00×10^{-1}	7.95×10^{-4}	1.30×10^{-3}	2.17×10^{-4}	9.16×10^{-4}	3.20×10^{-4}	8.85×10^{-6}	6.22×10^{-4}
6.761	1.94×10^{-1}	4.99×10^{-4}	9.15×10^{-4}	1.19×10^{-4}	8.75×10^{-4}	1.68×10^{-4}	5.60×10^{-6}	3.46×10^{-4}
8.423	1.12×10^{-1}	2.89×10^{-4}	5.89×10^{-4}	5.82×10^{-5}	3.05×10^{-4}	7.03×10^{-5}	2.92×10^{-6}	1.51×10^{-4}
10.106	6.08×10^{-2}	1.56×10^{-4}	3.53×10^{-4}	2.55×10^{-5}	1.49×10^{-4}	2.46×10^{-5}	1.26×10^{-6}	5.30×10^{-5}
11.883	2.80×10^{-2}	7.20×10^{-5}	1.78×10^{-4}	8.99×10^{-6}	5.72×10^{-5}	6.16×10^{-6}	3.77×10^{-7}	1.21×10^{-5}
13.585	1.79×10^{-2}	4.61×10^{-5}	1.2×10^{-4}	2.16×10^{-6}	1.47×10^{-5}	2.9×10^{-6}	1.9×10^{-9}	1.31×10^{-4}
15.415	3.55×10^{-3}	9.11×10^{-7}	2.2×10^{-4}	1.77×10^{-4}	1.11×10^{-4}	1.3×10^{-11}	7.7×10^{-11}	1.61×10^{-10}
17.360	3.99×10^{-3}	1.03×10^{-4}	1.3×10^{-4}	9.20×10^{-4}	3.00×10^{-10}	1.8×10^{-12}	2.9×10^{-15}	2.25×10^{-14}

* The equivalent volume ϕ' for silver nitrate = 40.87,
for ammonium nitrate = 46.41, and
for acetic acid = 57.2 ml.

The two columns headed *A* and *B*, under "Relative viscosity", refer to water = 1.0000 (*A*) and *N*/10 silver nitrate = 1.0000 (*B*). Further experimental results are given in the "Discussion of Results", where they occur more appropriately.

Discussion of Results

We can reasonably claim that our conductance figures are the best so far obtained for silver nitrate and for ammonium nitrate in the range of high concentration at 25°C. As experimental figures they therefore have their value and the same is true of our density and viscosity figures. The behavior of ammonium nitrate solutions seems to be anomalous or at least very different from that of silver nitrate solutions. The specific conductance (uncorrected for viscosity) passes through a maximum value, with increasing concentration, in the case of ammonium nitrate, but not of silver nitrate. The viscosity of ammonium nitrate solutions is less than that of water up to a concentration of 4 *N*, whereas that of silver nitrate solutions is always greater than that of water.

In Table II we have applied our data in various calculations, on the assumption of partial dissociation. Many of these calculations are mere "jeux d'esprit", since no one nowadays believes that the Ostwald dilution law, or any simple modification of it, can apply to the behavior of strong electrolytes, but there may be some advantage in the comparison of actual behavior with an ideal standard, just as there is in the comparison of actual gases with the ideal gas law. As a basis for the calculation of degree of dissociation we have taken the equivalent conductance and viscosity of *N*/10 solution (instead of the limiting conductance and the viscosity of water), since there seems no doubt that, up to this concentration, dissociation is complete and that the decrease in conductance is due to factors covered by the equations of Debye, Onsager, Shedlovsky, *et al.* The table contains data for the three electrolytes silver nitrate, ammonium nitrate, and acetic acid. The three values of α refer, first, to the simple conductance ratio, second, to that ratio multiplied by η , the ratio of the viscosity of the solution to that of the *N*/10 solution, and, third, to a conductance ratio for which the equivalent conductance has been calculated by multiplying the specific conductance by $\phi - \phi'$, as recommended by Walden, followed by multiplication by η as before. The three values of *K* are the Ostwald "constants", using the above values of α , and, in the third case, introducing into the Ostwald expression $\phi - \phi'$ instead of the dilution. The concentration range varies from 0.1 molar to 9.709 molar, in the case of silver nitrate, and from 0.1 molar to 11.282 molar in the case of ammonium nitrate. All figures refer to 25°C.

Table III contains data on the viscosity and density of a *N*/10 silver nitrate solution to which various amounts of sugar had been added.

TABLE III

VISCOSITIES AND DENSITIES OF *N*/10 SILVER NITRATE
CONTAINING CANE SUGAR, AT 25°C.

Grams cane sugar per 100 ml. solution	Density, gm./ml.	Viscosity relative to <i>N</i> /10 silver nitrate without sugar
0.00	1.011	1.000
2.00	1.019	1.055
4.00	1.027	1.115
6.00	1.034	1.177
8.00	1.042	1.243
10.00	1.050	1.308
15.00	1.069	1.533
18.00	1.080	1.699
21.00	1.091	1.880
24.00	1.102	2.100
30.00	1.126	2.633
34.00	1.140	3.117

The results of Table III were graphed and the sugar content corresponding to the viscosities of various molarities of silver nitrate (without sugar) read off. These solutions (of *N*/10 silver nitrate plus cane sugar) were then made up and their conductances determined at 25°C. The basis of experiment and calculation here is the hope that if two concentrations were compared at equal viscosity the difference in conductance might be solely, or largely, due to a difference in ionization. Table IV shows, however, that overcorrection appears again and α increases after about 6.0 molar. K_1 increases like K_2 and K_3 (of Table II). This work was not repeated with ammonium nitrate.

TABLE IV

EQUIVALENT CONDUCTANCES OF *N*/10 SILVER NITRATE CONTAINING
VARIOUS AMOUNTS OF CANE SUGAR AT 25°C.

Wt. cane sugar per 100 ml. solution	Corresponding molarity of silver nitrate	Equiv. cond. of <i>N</i> /10 AgNO ₃ plus sugar	Equiv. cond. of AgNO ₃ of column 2	Conductance ratio $= \frac{\Lambda}{\Lambda_{N/10 + \text{sugar}}}$
2.3	1.0	104.1	77.82	0.748
5.7	2.0	97.1	64.20	0.661
9.5	3.0	90.1	54.97	0.610
13.4	4.0	82.4	48.50	0.588
16.8	5.0	76.0	43.14	0.567
19.5	6.0	71.1	38.55	0.543
24.6	7.0	62.8	34.70	0.553
28.3	8.0	56.6	31.20	0.552
35.4	9.0	46.7	27.99	0.599

Following up the above idea, we now determined the viscosity of silver nitrate solution of various concentrations at a series of rising temperatures and thus interpolated for each concentration a temperature at which the viscosity

was the same as that of $N/10$ silver nitrate at 25°C . The density-viscosity-temperature data for each concentration are recorded in Table V.

TABLE V
DENSITIES AND VISCOSITIES OF SILVER NITRATE SOLUTIONS
AT VARIOUS TEMPERATURES

Normality	Temp. $^{\circ}\text{C}$.	Density, gm./ml.	Viscosity ($N/10$ AgNO_3 = 1.000)
1.0	25.0	1.137	1.065
"	28.0	1.136	1.002
2.0	25.0	1.276	1.167
"	32.6	1.271	1.000
3.0	25.0	1.413	1.295
"	32.6	1.407	1.126
"	39.0	1.402	1.002
3.98	25.0	1.544	1.459
"	39.0	1.537	1.129
"	46.5	1.530	1.001
5.0	25.0	1.685	1.643
"	47.0	1.668	1.134
"	55.9	1.663	0.994
5.97	25.0	1.810	1.873
"	55.9	1.791	1.128
"	66.5	1.786	0.995
6.95	25.0	1.943	2.151
"	66.5	1.923	1.149
"	79.0	1.908	1.000
7.96	25.0	2.075	2.483
"	79.0	2.046	1.145
"	94.8	2.033	0.995

In Table VI are given the equivalent conductances (experimental) for temperatures at which the viscosity equals that of $N/10$ silver nitrate at 25°C ., the conductance ratio, and K of the Ostwald dilution law.

TABLE VI
CONDUCTANCES OF SILVER NITRATE AT VARIOUS TEMPERATURES AND DERIVED DATA

Normality	Temp. $^{\circ}\text{C}$.	Equiv. cond.	$\alpha = \frac{\Lambda_c(t^{\circ})}{\Lambda_{0.1}(25^{\circ})}$	$K = \frac{\alpha^2 C}{1 - \alpha}$
1.0	28.00	82.2	0.754	2.311
2.0	32.60	73.2	0.671	2.738
3.0	39.1	69.9	0.641	3.435
4.0	46.5	68.6	0.629	4.264
5.0	55.9	68.9	0.626	5.240
6.0	66.3	69.8	0.640	6.826
7.0	79.0	71.4	0.655	8.708
8.0	94.8	74.3	0.681	11.577

It is apparent that, as with all other viscosity corrections, overcorrection results and K increases continuously.

Conclusion

We hold no brief for the view that ionization is incomplete in strong solutions but it is interesting to speculate on that possibility. We have produced no evidence that such is the case, beyond a remarkable agreement, in the case of ammonium nitrate, with the Walden formula, but this may receive some other explanation. All attempts to correct for viscosity have failed, presumably because the external viscosity is not a determining factor. If the ratio of the absolute velocities of the ions of the same electrolyte, under the same potential gradient but at different concentrations, can be determined, the question of complete or partial ionization will be solved; at least, if the ratio of the ion velocities does not turn out to be the same as the ratio of the conductances then some other influences are at work. We hope eventually to do this. Meantime, we are extending our conductance work to 95°C. and to temperatures above the melting points of the respective salts.

Acknowledgment

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THE PREPARATION OF SOME SUBSTITUTED BENZOPHENONES AND BENZOHYDROLS¹

BY JEAN P. PICARD² AND C. W. KEARNS³

Abstract

Six benzophenones and their corresponding benzohydrols have been prepared. The former were obtained through the extension of a method employed by Boeseken for the preparation of benzophenone dichloride by the action of carbon tetrachloride on benzene in presence of anhydrous chloride. The ketones obtained were subsequently reduced in good yields to the corresponding hydrols by means of aluminum isopropylate. Some of these compounds have been found to possess insecticide properties.

Introduction

The preparation of symmetrical halogen and alkyl substituted ketones from carbon tetrachloride was accomplished through the extension of a method suggested by Boeseken (1) in 1905 for the preparation of benzophenone dichloride by the action of carbon tetrachloride on benzene in the presence of anhydrous aluminum chloride. When these compounds were subsequently hydrolyzed by steam, the corresponding ketones were obtained.

This method seems to be more efficient than the process of condensing substituted benzoyl chlorides with halogen or alkyl derivatives of benzene. The latter method, according to Shopff (6), gives poor yields and the high temperature at which the reaction is carried out occasions deep-seated changes through the action of the aluminum chloride present. With carbon tetrachloride the condensation of monohalogenated and monoalkylated derivatives of benzene proceeds at room temperature without the formation of resinous by-products.

The reduction of the symmetrical aromatic ketones to the corresponding secondary alcohols may be accomplished by means of alcoholic alkali and zinc dust. The only drawback to this method is the formation of pinacol, which, according to Cohen (2) is the first step in the reduction, and that the proportions of secondary alcohols and pinacols are in direct relation with the stability of the latter towards alkali.

The aromatic ketones were reduced in satisfactory yields through the use of aluminum isopropylate. Since the proposal of this method by Meerwein and Schmidt (3) and by Ponndorf (5) for the reduction of carbonyl group to the corresponding alcohol an extensive amount of work with this method has been reported, but as yet nothing has been published on the application of this method to the symmetrical substituted aromatic ketones.

Except for 4, 4'-dimethoxybenzophenone all the other ketones, Table I, have been reduced in practically quantitative yield by this method. The aluminum

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alkoxide used as reducing agent was prepared according to the procedure given by Wilds (7, pp. 179-223).

Physical Properties

These compounds have been prepared in attempts to explain the essential structural features of DDT. Their relative toxicities have been reported by Picard and Kearns (4).

Experimental

(i) *R,R'*-Disubstituted Benzophenones

The equipment used for the preparation of the ketone derivatives consisted of a two-necked, round-bottomed flask, fitted with a Heshberg's stirrer, addition funnel, thermometer, and a reflux condenser connected to a gas trap for the removal of the hydrogen chloride evolved during the reaction. In certain cases external cooling was required to slow down the reaction.

4, 4'-Difluorobenzophenone

This ketone was prepared by adding 96 gm. (1 mole) of fluorobenzene to a mixture of 77 gm. (0.5 mole) of dry carbon tetrachloride, 134 gm. (1 mole) of anhydrous aluminum chloride, and 250 cc. of dry carbon disulphide. The reaction was allowed to proceed for three hours at room temperature.

The hydrolysis of aluminum chloride adduct was carried out by adding cracked ice to the reaction mixture. External cooling was used in order to speed the hydrolysis.

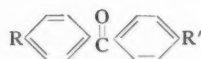
By treating the reaction mixture with steam, the excess of carbon disulphide was removed, leaving behind the 4, 4'-difluorobenzophenone dichloride which, on continuation of the heating for two hours, hydrolyzed to the corresponding 4, 4'-difluorobenzophenone. The solid residue was recrystallized from hot benzene and washed three times with 100-cc. portions of medium boiling petroleum ether. Ninety-four grams (85% of theory) of white crystalline plates melting at 102° to 103°C. was obtained. Its oxime was found to melt at 135° to 136°C. The 4, 4'-disubstituted benzophenones reported in Table I were prepared by the same procedure.

(ii) *R,R'*-Disubstituted Benzohydrols

In a 200 cc. round-bottomed flask were placed a solution of 20 gm. (0.1 mole) of aluminum isopropylate (or 100 cc. of 1 *M* solution in isopropyl alcohol) and 0.1 mole of the ketone to be reduced. A 25 cm. reflux condenser was attached to the flask, but the water in the cooling jacket was replaced by 3 cc. of methanol. At the top of the reflux condenser was attached, by means of a short, bent glass tube and cork stoppers, a small water-cooled condenser set for distillation. A boiling chip was added, and the solution was refluxed in an oil bath (temperature 120° to 125°C.) at a rate such that 5 to 10 drops of distillate were collected per minute.

TABLE I

R, R'-DISUBSTITUTED BENZOPHENONES



R, R'	Starting material	Formula	M.p., * °C.	Calcd., %		Found, %		Yield, %	Oxime, m.p., °C.
				C	H	C	H		
F	C ₆ H ₅ F	C ₁₃ H ₉ OF ₂	102-103	71.96	3.93	71.72	3.76	85	135-136
Cl	C ₆ H ₅ Cl	C ₁₃ H ₉ OCl ₂	144-145	62.17	3.20	61.91	3.01	90	142
Br	C ₆ H ₅ Br	C ₁₃ H ₉ OBr ₂	173-174	45.91	2.37	45.81	2.25	86	151-152
CH ₃	C ₇ H ₈	C ₁₃ H ₁₄ O	92-92.5	85.67	6.71	85.49	6.58	92.5	162
CH ₃ O	C ₇ H ₈ O	C ₁₃ H ₁₄ O ₂	142-143	74.36	5.82	74.11	4.75	91	133
H	C ₆ H ₆ †	C ₁₃ H ₁₀ O	47-48	85.68	5.53	85.06	5.32	89	141

* All melting points are uncorrected.

† Benzophenone was prepared according to a method submitted by C. S. Marvel and W. M. Sperry, *Org. Syn.*, Vol. 1, p. 95.

4, 4'-Difluorobenzohydrol

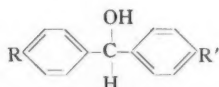
When 2.2 gm. (0.1 mole) of 4, 4'-difluorobenzophenone was refluxed with an equimolecular quantity of aluminum isopropylate, after three hours, a negative test for the presence of acetone was noted.

Then the excess of isopropyl alcohol was removed under slightly reduced pressure. The cooled residue was hydrolyzed by pouring it over a mixture of cracked ice and dilute hydrochloric acid (prepared from 35 cc. of concentrated hydrochloric acid and 175 cc. of water). The aqueous suspension was mixed well by swirling, to ensure complete hydrolysis. Extraction with ether and evaporation gave a brown oil that solidified at -10°C. The oil was transferred to a 50 cc. Claissen distilling flask. At 143°C., under 3 mm. of reduced pressure, 2 gm. (91% of theory) of a viscous transparent liquid came over, which, upon standing, crystallized. The melting point of this product was found to be 92° to 93°C. A search of the literature revealed no previous report of the preparation of this compound.

The procedure given above was followed in the preparation of the other benzohydrols reported in Table II.

TABLE II

R, R'-DISUBSTITUTED BENZOHYDROLS*



R, R'	Starting material	Formula	M.p., * °C.	Yield, %
F	C ₁₃ H ₉ OF ₂	C ₁₃ H ₉ OF ₂	92-93	91
Cl	C ₁₃ H ₉ OCl ₂	C ₁₃ H ₉ OCl ₂	89-90	92.5
Br	C ₁₃ H ₉ OBr ₂	C ₁₃ H ₉ OBr ₂	115-116	94
CH ₃	C ₁₃ H ₁₄ O	C ₁₃ H ₁₄ O	69	96
CH ₃ O	C ₁₃ H ₁₄ O ₂	C ₁₃ H ₁₄ O ₂	72	70
H	C ₁₃ H ₁₀ O	C ₁₃ H ₁₀ O	68	95

* All melting points are uncorrected.

Acknowledgments

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KINETICS OF THE OXIDATION OF TITANIUM¹

BY W. A. ALEXANDER² AND L. M. PIDGEON

Abstract

The rates of oxidation of titanium powder and sintered bar have been investigated in the temperature range 25° to 550°C. at pressures of 2 and 20 cm. oxygen maintained constant throughout each experiment. It has been shown that the oxidation process can be divided into two mechanisms, viz., the formation of a thin surface film and diffusion of oxide into the metal. The surface film formation at low temperatures follows the logarithmic equation:

$$\ln(t + 3) = k_1 V + k_2$$

on vacuum annealed metal surface. The diffusion process at higher temperatures is described by the equation:

$$\log \frac{C - C_f}{C_i - C_f} = -\text{const} - 2.3 \frac{t}{\tau}$$

after the initial oxidation. This equation leads to preliminary values of the diffusion constant of the order of 10×10^{-8} cm². per min. in the temperature range 463° to 565°C.

Introduction

The high melting point of titanium, its high strength, and its very good corrosion resistance at room temperature have pointed to the possibility of its use in the higher temperature ranges. It seemed advisable to approach the problem of this possible use of the pure metal or its alloys from the more theoretical side and to investigate the kinetics of oxidation of the pure metal as a basis for further work in the search for high temperature alloys.

Investigations on the oxygen-titanium system hitherto have been chiefly concerned with the solid solubility of the oxide (11), or the determination of the phases occurring (12, 24), and have paid scant attention to the rate of the oxidation process. Carpenter and Reavell (3) have carried out some experiments on titanium at relatively high temperatures and pressures of oxygen, but did not discuss the kinetics of the process. An investigation of the kinetics of oxidation of the closely related metal zirconium has been published by Gulbransen and Andrew (22) since the present experiments were completed. The gettering action of zirconium has been studied by Guldner and Wooten (23) and gave some indication of oxidation rates.

A considerable literature is available on the oxidation rates of other metals, e.g., zinc (38, 42), copper (6, 9, 43), nickel (42), iron (18, 19), stainless steel (19), magnesium (20), etc., including treatments of the kinetics of the process (8; 15, p. 71; 16, 17, 19, 21, 25, 29, 30, 31, 32, 39, 40, 41). The attack of metals by other gaseous agents, e.g., the halogens, sulphur, hydrogen sulphide, etc., also appears to follow rate laws similar to those for oxidation (36). For a short

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discussion of the theories of oxidation or tarnishing, and derivations of the three rate equations, linear, parabolic, and logarithmic, see Uhlig (37, p. 15).

Since oxygen or oxide of titanium is soluble in the metal the process of diffusion must also be considered. Literature on this subject is not so extensive, but theoretical and experimental work has been done (10; 27, Chapter 1; 28; 33; 34, p. 27), and some experiments on systems analogous to titanium and oxygen reported (7, 35).

An investigation of the rates of oxidation of titanium therefore appeared to be a desirable and promising problem, and the results have in large measure justified our expectations.

Experimental

Apparatus

Since the possibility of diffusion existed in the taking up of oxygen by titanium, it seemed preferable to operate at constant pressure and measure the amount taken up with time. Thus a constant concentration of oxygen should obtain at the surface of the metal. The variables to be investigated included temperature, pressure, surface condition, and specific surface.

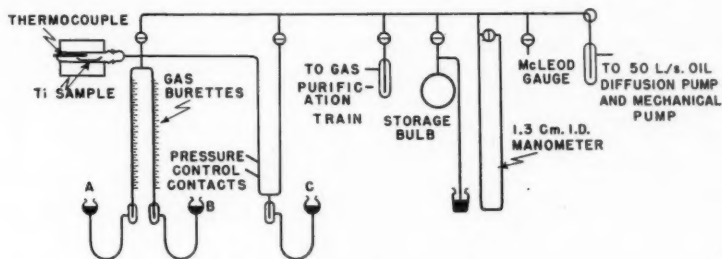


FIG. 1. Absorption apparatus.

The design of apparatus is indicated in Fig. 1. Pressure was controlled by a manostat arrangement operating motors which decreased the volume by raising mercury reservoirs *A* and *B* by a windlass arrangement. These volume changes were read on the gas burettes. According to Huntress and Hershberg (26) the sensitivity of such a control arrangement should be ± 0.15 mm. This sensitivity was usually exceeded by the use of a vacuum tube relay similar to that described by Huntress and Hershberg, which eliminated contamination by arcing at the tungsten-mercury surface. The volume of the absorption system and the sensitivity of control were such that at 2 cm. mercury operating pressure, the volume readings were accurate to ± 2.0 ml. This error is of course not cumulative.

The temperature was measured by a chromel-alumel thermocouple in a well in the reaction tube. The control sensitivity was about $\pm 2^\circ\text{C}$. The thermocouple was calibrated at the melting points of high purity tin, zinc, and aluminum.

Some care had to be given to the choice of a container owing to the high activity of titanium in the reduction of oxides. The stainless steel boat finally chosen showed no measurable absorption over long periods in oxygen at atmospheric pressure at 550°C. and showed no sign of reaction with the titanium powder.

Materials

The titanium used in this work was all taken from a composite lot prepared in this laboratory by the Kroll-Dean method (4, 5). Chemically pure titanium tetrachloride and high grade distilled magnesium were used, and the purity of the titanium was assumed to be similar to that described by Dean *et al.* (4). This was confirmed by analysis for gaseous impurities, by courtesy of Dr. N. P. Allen, National Physical Laboratories, England, which showed the following concentrations: O₂, 0.12; H₂, 0.05; N₂, 0.05%. Satisfactory quantitative methods of analysis for the very low concentrations of metallic impurities are not known.

The titanium was employed in two forms—powder and sintered bars made from this powder by standard powder metallurgy technique. The powder was all minus 30 mesh and the size distribution was very close to that noted by Dean *et al.* (4). The bars were prepared by pressing weighed lots of powder, moistened with alcohol to prevent segregation, at 50 tons per sq. in., and sintering *in vacuo* (0.2 micron or less) for 18 hr. at 1000°C. Some bars were of a grey metallic color with low reflectivity while later lots in the same apparatus under apparently identical conditions were quite bright. Hardness and forgeability were similar to those reported by Dean *et al.* (5). The weights of all samples used in this work, both powder and bars, were within 0.7% of 10 gm.

After the production process of washing and drying at room temperature, the powder samples were simply degassed at 311°C. in high vacuum (< 0.1 micron) in the early runs, and at 565°C. in the later runs. They were then cooled *in vacuo*, normally stood overnight *in vacuo*, were warmed to reaction temperature, and the oxygen admitted. The bars were not abraded but used as sintered. They were subjected to the same procedures of heating, degassing, and cooling *in vacuo* as the powder. No other procedure was adopted to remove the surface film before oxidation. According to Gulbransen and Andrew (22) it is impossible to prevent formation of a thin surface film on zirconium on cooling, even *in vacuo*, but our results would indicate that this film on titanium is unimportant compared to that formed at atmospheric pressure.

The oxygen used in these tests was generated in a small glass cell by electrolysis of 20% sulphuric acid and purified by passing over the following, in order: (1) calcium chloride, (2) soda lime, (3) platinized asbestos at 300° to 350°C, (4) sulphuric acid, (5) phosphorus pentoxide, and stored in a glass bulb sealed to the apparatus.

Experimental Results

Exploratory Runs

Preliminary experiments listed in Table I served to explore in a cursory way the behavior of the powder and massive metal under various conditions. (The missing run was vitiated by a leak.) The expectation that the absorption of oxygen would be readily measurable in the temperature range permissible in Pyrex was fulfilled. The general shape of the absorption curve with time is indicated by the first run, Fig. 2.

TABLE I
OXIDATION OF TITANIUM — EXPLORATORY EXPERIMENTS

Run No.	Ti form	Activation		Oxidation				Remarks
		Degassed at		O ₂ press., cm. Hg.	Temp., °C(±5°)	Time, min.	O ₂ absorbed, ml. N.T.P. per 10gm. Ti	
		Temp., °C.	Time, hr.					
1	— 30 mesh	25	1	2	330	428	16.2	
3	— 30 mesh	311	1	2	330	436	16.0	
4	Bar	311	1	2	330	432	1.2	
5				15	330	3010	2.6	Same bar — no further activation.
6		565	7	2	330	442	1.1	Same bar — re-activated.
7	— 30 mesh	413	2	2	330	432	23.1	
8	— 30 mesh	311	1	2	330	436	16.2	
					380	436	18.0	Same sample — no further activation.
					430	435	32.9	Same sample — no further activation.
		565	6	1.3-2	330	436	21.8	Same sample — reactivated.
9	— 30 mesh	311	1	20	330	436	12.5	
10	— 30 mesh	565	6	2	330	436	20.6	
					480	797	94	Same sample — no further activation. Preliminary diffusion test.

The excellent reproducibility of the runs is shown by comparison of Runs 1, 3, and 8 part I; 4 with 6; and 8 part IV with 10 part I, Table I.

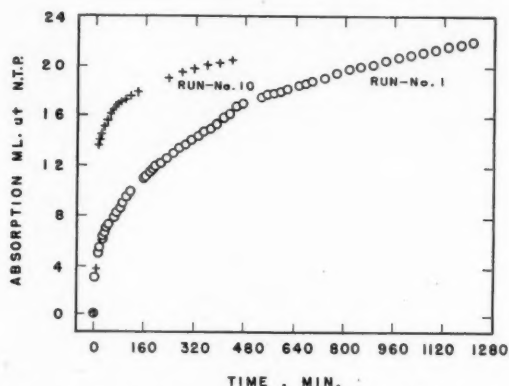


FIG. 2. Oxidation of titanium powder at 330°C. Effect of activation.

The importance of surface condition was shown very early in the work—compare Runs 7 and 10 part I with 3—when removal of surface film from the metal resulted in notable increase in amount of oxidation and distinct change in the shape of the rate curve as seen in Fig. 2, Run 10, part I.

Temperature increase produced a rapid increase in rate and amount of oxidation as shown by Run 8, Table I. High temperature absorption curves are also shown in Fig. 3.

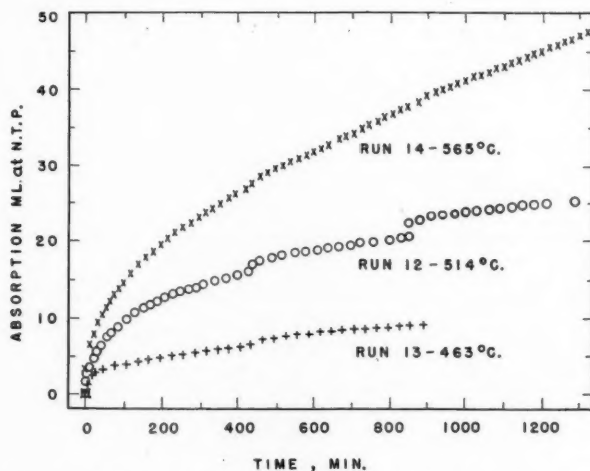


FIG. 3. Oxidation of titanium bar in diffusion range of temperature.

The effect of increased oxygen pressure is to reduce the absorption to about 3/4, as shown by Run 9 compared with, for example, Run 3, with no change in shape of the curve of number of milliliters absorbed vs. time.

The suggestion of Campbell *et al.* (2), and indirectly that of Guldner and Wooten (23), that the surface oxide film could be made to disappear by solution in the metal by heating at 550°C. *in vacuo* seemed to be verified, as will be seen by a comparison of Runs 4 with 6, and 10 with 8 part IV. The rate and amount of absorption is then, within reasonable limits, independent of the previous history of the sample.

It also was indicated from these experiments that the oxidation process could be divided into two steps or mechanisms, the formation of a surface film at relatively low temperatures with little or no diffusion into the body of the metal and oxidation at higher temperatures which would be limited by the rate of diffusion and extend over relatively long periods. The latter was indicated by Run 10 part II in the case of powder.

Tarnishing and Diffusion Runs

The experiments designed to investigate these two effects are summarized in Table II—the low temperature film formation in part I and the high temperature diffusion in part II. The shape of the absorption curves for the tarnishing action, part I, is the same as that of Run 10 plotted in Fig. 2, while

TABLE II

OXIDATION OF TITANIUM—TARNISHING AND DIFFUSION EXPERIMENTS
(All samples were activated by degassing for six hours at 565°C.)

Run No.	Ti form	Oxidation				
		O ₂ press., cm. Hg	Temp., °C. (±2°)	Time, min.	O ₂ absorbed ml. N.T.P./10 gm.	
11	— 30 mesh	2	25	437	3.2	Part I— Tarnishing
16	— 30 mesh	2	104	436	6.9	
15	— 30 mesh	2	156	443	9.8	
18	— 30 mesh	20	156	436	5.0	
17	— 30 mesh	2	207	436	12.8	
13	Bar	2	156	435	0.2 ₃	Part II— Diffusion
			463	435	6.4	
				890	9.2	
12	Bar	2	26	437	0.1 ₂	
			514	437	16.2	
				1286	25.6	
19	Bar	20	514	442	17.8	
				878	24.3	
				1313	30.1	
				1749	32.5	
14	Bar	2	565	436	27.5	
				876	38.4	
				1317	47.6	

typical absorption curves for the diffusion process are shown in Fig. 3. The curve for tarnishing shows a more rapid initial absorption than those for the diffusion process and an approach to zero rate, while diffusion would appear to continue for very long times.

The effect of temperature is considerably greater in the case of the diffusion type of oxidation than in the surface film formation or tarnishing, the increase in absorption by diffusion with 100° increase in temperature being about 4.5-fold from Runs 13 and 14, while the increase in tarnishing with 182° increase in temperature from 25°C. to 207°C. is just fourfold, as indicated by Runs 11 and 17.

The effect of pressure is distinctly different for the two actions. A decrease in amount of tarnishing to about 1/2 occurs with the tenfold increase in pressure, as seen from a comparison of Runs 15 and 18, while the diffusion rate is increased somewhat with increase in pressure, as shown by Runs 12 and 19.

An estimate of the surface area of the powder samples is also possible from the data of Table II. On the assumption that the tarnishing rate is proportional to the surface area, the powder would have, from a comparison of Runs 11 and 12, about 30 times the area of the bar, and from Runs 13 and 15, about 40 times. From the measured area of the bar (18.9 sq. cm.) the surface area of the powder would thus be about 57 to 76 sq. cm. per gm. This was confirmed in a qualitative way by an attempt to measure the surface area by the B.E.T. method.* The measurement showed that the surface area was too small to be measured with this apparatus. The lowest surface area measurement reported by Emmett (14, p. 95) is 0.2 sq. m. per gm., although recently (13, p. 82) areas as small as 100 sq. cm. have been determined by special procedures.

The assumption of a similar process with powder and bar is supported by the similar shape of oxidation curve and the fitting of the same logarithmic law to the data. This is more readily observed from runs without activation owing to the greater absorption by the bar at the higher temperature. Compare Runs 3 and 4, Fig. 6.

Discussion

Low Temperature Oxidation

The tarnishing action will be considered first. As mentioned above, an extensive literature exists on this subject and in most cases the rates seem to follow the parabolic equation $V^2 = kt$ reasonably well (8, 18, 19, 21, 29, 40). However, the logarithmic rate equation is found to apply in a number of cases (36, 38, 43). Further, some cases are known where both equations apply to different stages in the oxidation of the same metal (6, 18).

* This measurement was made through the kind co-operation of Dr. E. L. Tollefson of the National Research Laboratories, Ottawa.

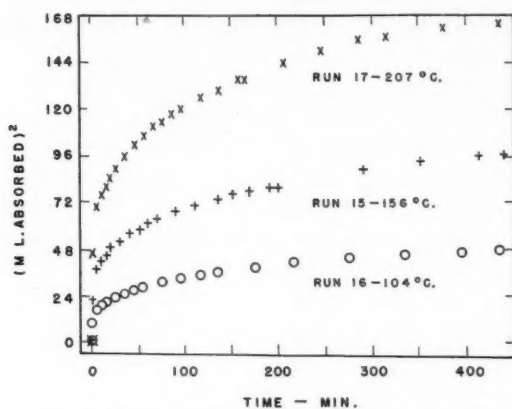


FIG. 4. Tarnishing of titanium powder. Test of parabolic rate equation.

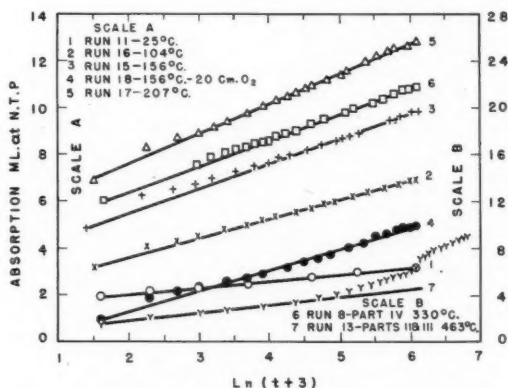


FIG. 5. Tarnishing of titanium. Logarithmic equation. Run 13—Bar titanium, others —30 mesh powder.

We have applied the parabolic equation to these results with no notable success, as seen in Fig. 4, i.e., no change in shape of curve from plot of volume absorbed vs. time, while, as may be seen from Fig. 5, the logarithmic equation

$$\ln(t+3) = k_1V + k_2 \quad (1)$$

produces a reasonable approach to a straight line. Here t is time in minutes, V is total volume absorbed, and k_1 , k_2 are constants. A small deviation from this line in the sense of a greater volume absorbed occurs in most runs in the early stages. This is undoubtedly due to the addition of 3 units to time t , since the plot of $\ln t$ vs. volume gives a smooth curve slightly concave upwards. The constant 3 was chosen arbitrarily, the justification being that the equation fitted the data from room temperature to 200°C. under present experimental conditions. A similar equation was applied by Dighton and Miley (6) in the case of the oxidation of copper: $V = k \ln(a(t+t') + 1)$. The equation of

Vernon *et al.* (38), $V = k \log (at + 1)$, may be simply rearranged to account for such a constant, viz.,

$$V = k \log \left[a \left(t + \frac{1}{a} \right) \right].$$

A second constant is necessary to account for the intercept of the y-axis.

The constants k_1 and k_2 in Equation (1) vary with temperature while the number 3 does not change. The theory of this type of oxidation is too uncertain to permit attaching much physical significance to this variation. It is to be noted, however, that the constants vary in a regular manner with temperature.

As may be seen from Fig. 5 (Run 18) the effect of increased pressure is to decrease the total amount absorbed (18) without affecting the nature of the process, since the logarithmic equation still applies.

At higher temperature, the deviation of the graph from a straight line for Run 13 of number of milliliters absorbed vs. $\ln(t + 3)$ in Fig. 5 may be considered an indication of a change in the nature of the absorption process, when diffusion becomes significant. On this basis, diffusion is not important at 330°C. since Run 8 part IV, Fig. 5, fits the low temperature equation. Initial runs at this temperature but with no surface activation obey Equation (1) for the tarnishing action but with a change in the constant 3 to 30, as shown in Fig. 6. It should also be noted that by further changes in this constant, dependent on temperature, Equation (1) may be fitted to the initial stages *only* of the higher temperature diffusion runs, i.e., presumably to the formation of the surface film of titanium dioxide.

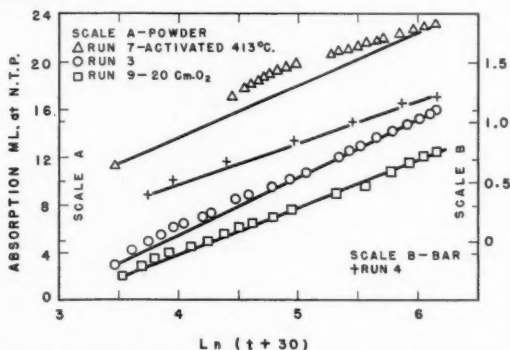


FIG. 6. Oxidation at 330°C. Modification of logarithmic equation for unactivated titanium and deviation from modification on activation—Run 7.

It may thus be concluded that the rate of low temperature surface oxide film formation on an annealed titanium surface follows a logarithmic law similar to that found for zinc and copper. A change in the metal surface condition or the beginning of diffusion results in a departure from this law owing to a change in the nature of the process.

High Temperature Oxidation

The standard diffusion equations in a concentration gradient (33) have been worked out for the case of diffusion into a semi-infinite body across a phase boundary (7; 34, p. 27; 35). These equations then result in a logarithmic type equation relating concentrations with the diffusion constant (34, p. 28; 35):

$$\log \frac{C - C_f}{C_i - C_f} = -\text{const} - 2.3 \frac{t}{\tau}, \quad (2)$$

where C is oxygen concentration in per cent by weight, C_f final concentration which we have set equal to TiO_2 (3), C_i the initial concentration in metal = 0.12%, t = time, and $\tau = \frac{a^2}{\pi^2 D}$, when a = side of equivalent cube, cm., D = diffusion coefficient, sq. cm. per min.

This equation appears to fit the results—giving, as predicted (10, 28), essentially a straight line in the later stages of the run. The results of such calculations are shown in Fig. 7 for Runs at 463°, 514°, and 565°C. The breaks in some of the curves at 436 min., 872 min., etc., are due to cooling the sample at the end of a day's run, when additional absorption took place with some desorption on warming again. However, the slopes of the later parts of the curves are in reasonable agreement within each run. A plot of the square of volume of gas absorbed vs. time for Run 12 showed that the parabolic law is not applicable to absorption at these temperatures.

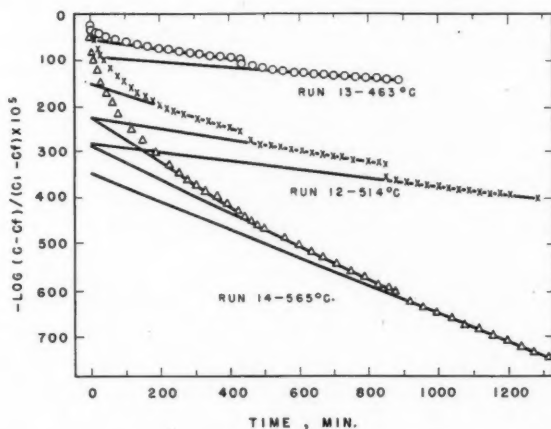


FIG. 7. Diffusion of oxygen in bar titanium—slope = $-2.3 \times \frac{\pi^2 D}{a^2}$.

A tenfold increase in pressure in Run 19 produced only a slight difference from Run 12 in amount and rate of absorption, as indicated in Table II. Thus the effect of pressure is in line with our assumption of constant surface con-

centration equal to titanium dioxide. The plot of Equation (2) for this run is very close to that of Run 12 and leads to a similar final value for the diffusion constant, as seen in Table III.

TABLE III
DIFFUSION CONSTANTS

Temp., °C.	O ₂ pressure	O ₂ Conc'n., % by wt. at end of				Diffusion const., cm ² /min. × 10 ⁹			
		Part 1	Part 2	Part 3	Part 4	Part 1	Part 2	Part 3	Part 4
463	2	0.21	0.25			8.4	4.7		
514	2	0.35	0.42	0.49		12.5	9.6	7.6	
514	20	0.38	0.47	0.55	0.59	30	12.3	12	7
565	2	0.52	0.66	0.80		40	29	24	

The graph of Equation (2) leads to a value of the diffusion constant for each straight portion of the curve. These calculated values are collected in Table III. The decrease in slope with increasing time may be safely assumed to be due to insufficient time to reach equilibrium conditions, rather than to limited depth slowing down diffusion by decreasing the concentration gradient. This conclusion is supported by tests in another connection where titanium samples of similar size were oxidized at 1000°C. over comparable periods of time. Metallographic examination after vacuum quenching in oil indicated a relatively thin layer of oxide solution around the surface of the specimen. An oxide layer about 0.1 mm. thick formed in air at 927°C. is also mentioned in the discussion of a paper by Brace (1, p. 142). Hence more weight should be given diffusion constants calculated from the later stages of the run. It is well known that the diffusion constant is dependent on concentration (35) but Table III shows no regular variation with concentration and apparently the levels of concentration are too low to have any effect.

According to theory, measurement of the slope of the curve of $\ln D$ vs. $\frac{1}{T}$ should yield the activation energy of the diffusion process. However, the values in Table III show too much variation to permit an estimate to be made with much accuracy. As mentioned by Jost (27, p. 15), however, even rough estimates of the diffusion constant can be valuable, and our values are presented as approximations within about an order of magnitude. The work is being continued and extended to higher temperatures; more accurate values should then be obtained.

The present experiments have shown that a surface film of oxide forms rapidly on titanium while diffusion is relatively a much slower process. This is suggested as the explanation of Hickman and Gulbransen's (24) finding only titanium dioxide and no lower oxides, on the surface of titanium in contact

with oxygen at 300° to 700°C., rather than a failure of titanium to reduce titanium dioxide, or of titanium ions to form and diffuse into the oxide layer.

Similar rates of oxidation of titanium and zirconium are to be expected from their close similarity in many other properties. This is substantiated by a comparison of the results of Gulbransen and Andrew (22) for the oxidation of zirconium with the present experiments on titanium. The rates of oxidation under similar conditions of surface pretreatment, temperature, and pressure agree within a factor of about two. Gulbransen and Andrew apparently did not remove the film formed in air at room temperature, which may explain their failure to find agreement with a logarithmic equation. The shape of the zirconium oxidation curves is also closer to those for unactivated than activated titanium. The effect of pressure at 375°C was similar to the higher temperature effect with titanium, but a test at low temperature was not made with zirconium. The value of the diffusion constant for zirconium also was only about an order of magnitude greater than that found for titanium.

Oxidation experiments in these laboratories since the completion of the above work, on titanium from another source, have indicated that impurities (and porosity) have a large effect on the oxidation rates. Similar results have been reported by Brace (1, p. 142) on titanium remelted in thoria.

Conclusions

(1) Up to about 300°C. the oxidation of titanium results in the formation of a thin surface film and oxygen absorption is limited.

(2) At about 450°C. and above, diffusion begins, with oxidation continuing over long periods.

(3) The rate of the low temperature oxidation or tarnishing follows the known logarithmic equation:

$$\ln(t + 3) = k_1 V + k_2. \quad (1)$$

(4) The constant added to the time in Equation (1) is influenced by the surface condition but not by temperature or pressure in the tarnishing range. The constants k_1 and k_2 vary regularly with temperature and pressure.

(5) Diffusion rates follow the equation:

$$\log \frac{C - C_f}{C_i - C_f} = -\text{const.} - 2.3 \frac{t}{\tau} \quad (2)$$

in the range of temperature and pressure investigated.

(6) Diffusion constants of the order of 10×10^{-8} cm². per min. have been found for the formation of titanium - titanium oxide solid solution.

Acknowledgments

This work has been sponsored by the Associate Committee on High Temperature Metals of the National Research Council of Canada, whose financial assistance and permission to publish is hereby gratefully acknowledged.

The co-operation of the staff of the Metallurgy Department of the Ontario Research Foundation in pressing the bars and obtaining the analysis of the titanium powder is also greatly appreciated.

Note

Since the present work was submitted for publication, a paper by E. A. Gulbransen and K. F. Andrew on the "Kinetics of the Reactions of Titanium with O_2 , N_2 and H_2 " has appeared in the October 1949 issue of the Journal of Metals. The scope of the work and the interpretation of the results differ considerably in the two papers. The experimental results and calculated data agree in some instances but differ considerably in others.

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**β -AROYL- α,β -DIPHENYLPROPIONIC ACIDS FROM
DIPHENYLSUCCINIC ANHYDRIDE¹**

BY JOHN A. MCRAE, ROBERT A. B. BANNARD, AND RONALD B. ROSS

Abstract

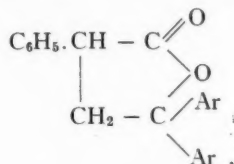
β -Aroyl- α,β -diphenylpropionic acids have been prepared in good yields from diphenylsuccinic anhydride either by the Friedel-Crafts' or by the Grignard reaction. The latter served also for the determination of the orientation of the acids produced in the Friedel-Crafts' reactions. Reduction of the aroyl acids was studied using the Clemmensen, high pressure hydrogenation and Meerwein-Ponndorf methods.

Like so many other β -aroylpropionic acids β -aroyl- α,β -diphenylpropionic acids have some interest as substances from which polynuclear structures can be formed through the well established procedures of reduction, cyclization, and dehydrogenation. The only acid of this type so far described is β -benzoyl- α,β -diphenylpropionic acid first prepared by Reimer and Reynolds (11) and more recently by Crawford (3) by a much improved scheme starting from the action of the sodio-derivative of desoxybenzoin on ethyl α -bromophenylacetate. Crawford (4) reduced the acid to α,β,γ -triphenylbutyric acid by the Clemmensen method, although in rather meager yield, and from this synthesized 2,3-diphenylnaphthalene. Bergmann, Eschinazi, and Schapiro (1), recognizing this poor yield, prepared triphenylbutyric acid by quite a different method, and later, when larger quantities were required, Crawford *et al.* (5) preferred making this acid from α,β,γ -triphenylbutyric nitrile, which was more readily available. Although the reported yield on the Clemmensen reduction of β -benzoyl- α,β -diphenylpropionic acid is disappointing, we have thought it desirable to study the production of this and other β -aroyl acids which it could be expected would be formed from diphenylsuccinic anhydride by the application of either the Friedel-Crafts' reaction or Grignard reagents.

Diphenylsuccinic anhydride reacts readily in the Friedel-Crafts' reaction with benzene to give the expected β -benzoyl- α,β -diphenylpropionic acid in 75% yield of the two isomers. Toluene reacted to give an 86% yield of β -*p*-toluyl- α,β -diphenylpropionic acid. With *o*-xylene in nitrobenzene the 3,4-dimethylbenzoyl acid was obtained but using naphthalene in the same solvent or in tetrachloroethane only very small yields of the β -1-naphthoyl- and β -2-naphthoyl acids could be obtained. Anisole reacted well to give the β -*p*-anisoyl acid but in view of the results of Robinson and Young (12) with veratrole and phenylsuccinic anhydride it was somewhat surprising to find that this ether and diphenylsuccinic anhydride gave only an insignificant amount of acidic material. On the other hand this result may be compared with those of Fieser and Daudt (6), who obtained poor yields of ketonic acids when α,α' -dimethylsuccinic anhydride was used in the Friedel-Crafts' reaction.

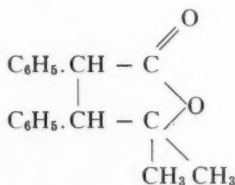
¹ Manuscript received June 23, 1949.
Contribution from the Department of Chemistry, Queen's University, Kingston, Ont.

The orientation and identity of these keto acids was more easily ascertained by direct comparison with the ketonic acids prepared by the action of the appropriate Grignard reagent on diphenylsuccinic anhydride than through oxidation experiments. Some years ago Komppa and Rohrmann (7) and a little later Weizmann, Blum-Bergmann, and Bergmann (14) described the conditions by which succinic anhydride will react with a molecular proportion of aryl Grignard reagents to give β -aroilpropionic acids. Although the latter authors could obtain only lactones from phenylsuccinic anhydride and aryl



Grignard reagents Fieser and Daudt (6) have shown that α,α' -dimethylsuccinic anhydride and the Grignard reagents from α - and β -bromonaphthalene give good yields of ketonic acids. Similarly, diphenylsuccinic anhydride has now been found to react well with the Grignard reagents from bromobenzene, *p*-bromotoluene, 4-bromo-*o*-xylene *p*-bromoanisole, and α - and β -bromonaphthalene to give good yields of the respective ketonic acids. This method is superior to the Friedel-Crafts' in those cases where nitrobenzene or tetrachloroethane must be used as a solvent.

A preliminary experiment with excess methylmagnesium iodide and diphenylsuccinic anhydride gave the lactone of γ -hydroxy- γ -methyl- α,β -diphenyl-*n*-valeric acid,



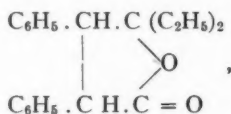
Considerable attention was given to the reduction of these keto acids in an effort to prepare α,β,γ -triphenylbutyric acid particularly in quantity. As was found by Crawford β -benzoyl- α,β -diphenylpropionic acid gave poor yields of α,β,γ -triphenylbutyric acid when reduced either by the Clemmensen method or Martin's modification of it. The methyl ester also failed to give significant yields by the Clemmensen reduction. Heating the acid with zinc dust and caustic soda likewise gave poor yields of triphenylbutyric acid. Towards the close of this work we were able to make some experiments using high pressure hydrogenation, thanks to the kindness of Dr. R. H. Manske. Using a pressure of 3650 p.s.i. and a copper chromite catalyst we found to our surprise that using β -benzoyl- α,β -diphenylpropionic acid the lactone of γ -hyd-

roxy- α,β,γ -triphenylbutyric acid was produced. This lactone has a melting point of 153°C^* and at first it was thought that the substance was one of the several forms of triphenylbutyric acid described by Crawford, namely, that of the same melting point, but the analytical results obtained from two other laboratories as well as a mixed melting point determination with a sample of triphenylbutyric acid, m.p. 153°C ., kindly supplied by Dr. Crawford showed that the two substances were quite different. Before the idea that our substance was triphenylbutyric acid was discarded, several ineffective attempts had been made to esterify it, including reaction with diazomethane.

On the other hand β -anisoyldiphenylpropionic acid was hydrogenated in the same apparatus and under similar conditions to α,β -diphenyl- γ -anisylbutyric acid, with excellent yield.

The reduction of ethyl α -phenyl- β -benzoylpropionate to γ -(α,γ -diphenyl- γ -butyric) lactone in high yield by aluminum isopropoxide in the Meerwein-Ponndorf method has been described by Bergmann, Eschinazi, and Schapiro (1). They showed further that this lactone could be reduced very successfully with phosphorus and hydriodic acid. We applied the same method to the methyl ester of β -toluyl- α,β -diphenylpropionic acid and obtained an 82% yield of α,β -diphenyl- γ -*p*-tolylbutyrolactone. This lactone was reduced in 52% yield to α,β -diphenyl- γ -*p*-tolylbutyric acid by heating with phosphorus and iodine in acetic acid solution.

In the hope of obtaining lactones which might be amenable to this latter treatment some experiments were made on the action of ethylmagnesium iodide on diphenylsuccinic ester. Using one, two, and five molecular proportions it was only in the last instance after long continued heating that much action occurred and a poor yield of the lactone of γ -hydroxy- α,β -diphenyl- γ -ethylcaproic acid,



was obtained.

The action of diphenylsuccinyl chloride on benzene in the Friedel-Crafts' reaction was found to give bidesyl, α,α' -diphenyldibenzoylthane, derived from the symmetrical form of this chloride. No evidence of the substance reacting in the isomeric, unsymmetrical form was obtained.

Experimental

Diphenylsuccinic Anhydride

Diphenylsuccinonitrile was prepared according to the directions of Lapworth and McRae (8) as modified by Brand and Loehr (2). Portions of the nitrile

* Melting points are corrected.

were hydrolyzed, some by the procedure of Lapworth and McRae, others by the later modification of Wawzonek (13). The latter seemed better adapted to the preparation of large amounts of diphenylsuccinic acid but higher yields were given in the former method. The acid was purified through its sodium salt, followed by recrystallization from alcohol or glacial acetic acid.

Fifty grams of diphenylsuccinic acid was heated under reflux with 150 ml. of glacial acetic acid and 100 ml. of acetyl chloride until all of the acid had dissolved. The solvent was removed first by heating on the water bath under reduced pressure and later by heating to 130° C. at 18 mm. The residue was distilled at reduced pressure (12 mm.) whereupon the anhydride distilled at 235° to 240° C. as a viscous pale yellow oil which solidified on the addition of a little chloroform. The crystalline mass was washed with anhydrous ether and could then be used directly. The yields were from 80 to 87%.

α,β -Diphenyl- β -benzoylpropionic Acid

Thirty grams of diphenylsuccinic anhydride was added in portions to a suspension of 40 gm. of aluminum chloride in 185 cc. thiophene-free benzene at room temperature. The mixture was stirred mechanically for six hours and allowed to stand overnight. Ice and dilute hydrochloric acid were added and the excess benzene removed by steam distillation. The residual material after drying was extracted with chloroform to obtain the desired acid. Evaporation of the solvent was followed by recrystallization of the acid from benzene, when a yield of 23.3 gm. or 74.5% of purified acid was obtained. On further recrystallization from alcohol the higher melting diastereoisomer, m.p. 210.5° to 211° C., separated, followed on dilution by the lower melting form, m.p. 201° to 202° C. The higher melting form was analyzed. Calc. for $C_{22}H_{18}O_3$: C, 79.97; H, 5.49%. Found: C, 79.44; H, 5.52%. Equivalent:—Calc: 330. Found: 326.

The lower melting diastereoisomer of this acid was obtained by adding the Grignard reagent from 14.7 gm. bromobenzene and 2.12 gm. magnesium to a suspension of 20 gm. diphenylsuccinic anhydride in 200 ml. ether. The mixture was mechanically stirred and refluxed during the addition which lasted 2.5 hr. Refluxing and stirring were continued for an additional three hours. After the reaction mixture had been decomposed, 21.1 gm. of acidic material (80.7%) was obtained which on recrystallization from ethyl acetate gave the pure acid, m.p. 200.5° to 201.5° C. The methyl ester was prepared in the usual way and recrystallized from ethyl alcohol, m.p. 147° C. Calc. for $C_{23}H_{20}O_3$: C, 80.19; H, 5.85%. Found: C, 80.6, H, 5.71%.

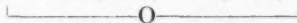
Reduction of α,β -Diphenyl- β -benzoylpropionic Acid

(a) *Clemmensen's method*.—Twenty-five grams of this acid was refluxed for 145 hr. with amalgamated zinc and hydrochloric acid. Some dibenzyl collected in the condenser. The yield of triphenylbutyric acid, m.p. 137° to 138° C., after separation from unchanged acid and other products was 20%.

(b) *Martin's modification of the Clemmensen method.*—Ten grams of the keto acid was heated under the conditions used by Martin. The yield of α,β,γ -triphenylbutyric acid was 30%.

(c) *Zinc dust and alkali.*—Ten grams of the keto acid was dissolved in an excess of 10% sodium carbonate solution (100 ml.), 20 ml. of 50% caustic soda was added, and to the hot solution 15 gm. of zinc dust was added in small portions. The mixture was refluxed for 20 hr. After removal of unchanged zinc and acidification, the product required very considerable treatment before pure triphenylbutyric acid could be obtained. Yield, 20%.

(d) *High pressure hydrogenation.*—Six grams of the keto acid was dissolved in 9.8 ml. of 15% caustic soda plus 50 ml. of water and then rendered neutral to litmus by the cautious addition of dilute hydrochloric acid. The solution was shaken with 1.0 gm. copper chromite catalyst prepared according to the directions of Adkins and shaken in an atmosphere of hydrogen for 20 hr. at 160° C. and at a pressure of 3650 p.s.i. The solution was treated with norite and acidified with hydrochloric acid. The weight of dry crude acid was 4.86 gm. (81%). Three recrystallizations from ethanol gave a product with a melting point of 153° C. This was at first thought to be α,β,γ -triphenylbutyric acid of the same melting point as described by Crawford, but on mixing it with an authentic sample of this acid a depression of 15° in the melting point was noted and the crystalline forms were quite different. The conclusion was reached that the substance is the lactone of γ -hydroxy- α,β,γ -triphenylbutyric acid, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}(\text{C}_6\text{H}_5)\text{CO}$. Calc. for



Found: C, 84.23, 84.20; H, 5.75, 5.94%. Equivalent calc.: 314. Equivalent found: 316.6. The end point in the titration was reached much more slowly than in the titration of the keto acid or triphenylbutyric acid. Before it was decided that the substance was a lactone, efforts made to esterify the supposed acid by methanol-sulphuric acid and by diazomethane gave back the unchanged substance.

α,β -Diphenyl- β -*p*-toluylpropionic Acid*

To a cold, mechanically stirred mixture of 20 gm. of diphenylsuccinic anhydride and 105 cc. of sulphur-free toluene 27.3 gm. of aluminum chloride was added in small portions over 2½ hr. so that the temperature remained at 3° to 5° C. The dark reddish brown solution so obtained was allowed to stand at room temperatures for 20 hr. and was then decomposed with ice and hydrochloric acid. The excess toluene was removed by steam distillation and the residual amorphous material digested with 5% sodium carbonate solution. This filtrate on acidification gave 23.6 gm. or 86.1% of the calculated yield of acidic product. The substance was recrystallized repeatedly from ethyl acetate and obtained as stout transparent needles, m.p. 232° to

* The orientation of this acid was established by its synthesis from *p*-tolylmagnesium bromide and diphenylsuccinic anhydride.

233° C. Found: C, 80.02, 79.98; H, 5.86, 5.98%. Calc. for $C_{23}H_{20}O_3$: C, 80.19, H, 5.85. Equivalent:—Found: 347.9. Calc. 344.4.

*Methyl α,β -Diphenyl- β -*p*-toluylpropionate*

This was obtained in high yield by refluxing the acid (5 gm.) with methanol (60 ml.) and sulphuric acid (12 ml.). It was recrystallized from methanol and obtained as needles, m.p. 154° C. Calc. for $C_{24}H_{22}O_3$: C, 80.4, H, 6.19%. Found: C, 80.52; H, 6.35%. An attempt was made to reduce this substance by Martin's (9) modification of the Clemmensen method. Five grams of the ester was heated for 72 hr. under reflux with 100 gm. of amalgamated zinc, 75 cc. of water, 190 cc. of concentrated hydrochloric acid, 100 cc. of sulphur-free toluene, and 5 cc. glacial acetic acid, the concentrated hydrochloric acid being replenished every six hours and the amalgamated zinc each 24 hr. The ester was recovered unchanged almost quantitatively.

*α,β -Diphenyl- γ -*p*-tolyl- γ -butyrolactone*

The foregoing ester (18 gm.) was reduced successfully to this lactone through the application of the Meerwein-Ponndorf method by heating according to the usual technique with 30 gm. of aluminum isopropoxide and 75 cc. isopropanol (dried over quicklime). After removal of the solvent at the end of the reduction the residue made into a paste with water was decomposed very slowly with ice cold concentrated sulphuric acid (130 cc.), so that the temperature remained between 0° and 10° C. The mixture was heated on the steam bath, filtered from insoluble material, and extracted with carbon tetrachloride. Recrystallization of the product from ethanol gave 13.5 gm. (82% of the theoretical) of α,β -diphenyl- γ -*p*-tolyl- γ -butyrolactone, m.p. 171.0° to 171.6° C.; transparent needles. The substance gave no color in the cold with concentrated sulphuric acid. Calc. for $C_{23}H_{20}O_2$: C, 84.10; H, 6.14%. Found: C, 83.92, 84.02; H, 5.94, 5.97%.

*α,β -Diphenyl- γ -*p*-tolylbutyric Acid*

An attempt was made to reduce 5 gm. of the foregoing lactone by heating with 3 gm. of red phosphorus and 25 cc. of freshly prepared constant-boiling hydriodic acid but after refluxing the mixture for six hours the lactone was recovered unchanged.

The lactone was reduced by heating 5 gm. of it for eight hours under a reflux condenser with a mixture of 1 gm. of iodine, 3 gm. of red phosphorus, 1 cc. of water, and 50 cc. of glacial acetic acid. After dilution and removal of the iodine with sodium bisulphite, the product which separated was dissolved in sodium carbonate solution. Acidification of this solution gave 2.6 gm. or 52% of theoretical yield of the acid. Several recrystallizations from alcohol gave the acid as silky needles, m.p. 177.5° to 178° C. Most of the unconverted lactone was recovered. Calc. for $C_{23}H_{22}O_2 \cdot C_2H_5OH$: C, 79.75; H, 7.50%. Found: C, 79.66, 79.64; H, 7.39, 7.31%. The substance gave no color in the cold with concentrated sulphuric acid.

α,β -Diphenyl- β -4-(1,2-dimethylbenzoyl)propionic acid $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{H}$

Twenty-four grams of pulverized aluminum chloride was added slowly at room temperature with mechanical stirring to a suspension of 20 gm. of diphenylsuccinic anhydride in 9.3 gm. of *o*-xylene and 60 ml. of tetrachloroethane. Stirring was continued for $2\frac{1}{2}$ hr. after the addition had been completed. The mixture was decomposed with ice and hydrochloric acid and the tetrachloroethane removed by steam distillation. The residue was then extracted with hot 10% sodium carbonate solution. Acidification of the extract gave 26.6 gm. of crude product, which by repeated crystallizations from ethyl acetate gave the pure substance of melting point 245.3° to 246.3°C . Calc. for $\text{C}_{24}\text{H}_{22}\text{O}_3$: C, 80.41; H, 6.2%. Found: C, 80.40; H, 6.24%. Equivalent calc: 358.4. Equivalent found: 361.5. The acid reacts with concentrated sulphuric acid almost precisely like its benzoyl and toluyl analogues, namely, it dissolved in the cold giving a rich ruby-red solution unchanged on heating to 100°C .

The same substance was prepared by reacting the Grignard reagent made from 21 gm. 4-bromo-*o*-xylene and 2.12 gm. magnesium turnings with 20 gm. diphenylsuccinic anhydride. On decomposing the reaction mixture 20.7 gm. of a pale yellow amorphous acidic material was produced. This on repeated recrystallizations from ethyl acetate gave the expected acid, m.p. 245°C ., which did not depress the melting point of the acid obtained from the Friedel-Crafts' reaction. Found: C, 80.23; H, 6.15%.

Methyl α,β -Diphenyl- β -4-(1,2-dimethylbenzoyl)propionate

This ester was prepared similarly to those already described. It was obtained in octahedra from methanol, m.p. 174.4° to 174.8°C . Calc. for $\text{C}_{25}\text{H}_{24}\text{O}_3$: C, 80.64, H, 6.46%. Found: C, 80.8, H, 6.28%.

α,β -Diphenyl- β -1-naphthoylpropionic acid and α,β -Diphenyl- β -2-naphthoylpropionic acid, $\text{C}_{10}\text{H}_7\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{H}$

A finely ground mixture of 20 gm. of diphenylsuccinic anhydride and 15.9 gm. naphthalene was added with good mechanical stirring over a period of one hour to 22 gm. anhydrous aluminum chloride dissolved in 70 ml. of freshly distilled nitrobenzene. The reaction temperature was kept at 0° to 3°C . during the addition and at 0° to 10°C . during an additional two hour period in which stirring was continued. After standing thirty-six hours the mixture was decomposed by the addition of ice and hydrochloric acid and the nitrobenzene removed by steam distillation. The viscous residue was heated with sodium carbonate and the nonacidic material removed. On acidification, 21.5 gm. of crude acidic product was obtained. This was either dissolved in ammonia, heated with charcoal, and the acidic material obtained after reacidification subjected to fractional crystallization from methanol, or crystallized directly. Two products were obtained, the less

soluble being the 1-naphthoyl acid and the more soluble the 2-acid. By repeated recrystallizations in which much material was lost 1.15 gm. of the 1-naphthoyl acid was obtained as colorless needles, m.p. 226° to 226.8° C. Calc. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30%. Found: C, 82.17; 81.91; H, 5.33; 5.21%. Equivalent calc. 380.4. Equivalent found: 377.7. The 2-isomer was obtained (0.22 gm.), by recrystallization from ethanol, as long needles, m.p. 259.5° to 260.5° C. Found: C, 81.98; H, 5.34%. Both of these acids were obtained using the Grignard reagent from α - and β -bromonaphthalene.

The Grignard reagent prepared by the action of 4.24 gm. of magnesium turnings on 27 ml. of α -bromonaphthalene in 100 ml. of ether was mixed with 120 ml. of anhydrous benzene and added with mechanical stirring over three hours to a suspension of 40 gm. diphenylsuccinic anhydride in ether with refluxing. The stirring and refluxing were continued for an additional three hours. After the mixture was decomposed with ammonium chloride the gummy precipitate that separated was collected, dissolved in sodium carbonate, and the acid precipitated. Yield of crude material, 35.6 gm. or 59%. Recrystallization from methanol gave a product identical with that formed in the larger amount in the Friedel-Crafts' reaction, m.p. 226° to 227° C. It did not depress the melting point of the latter substance.

Using in a similar manner the Grignard reagent from 19 gm. of β -bromonaphthalene on 20 gm. diphenylsuccinic anhydride, 25.7 gm. or 85% of crude acid was obtained which was recrystallized from ethanol and in another run from glacial acetic acid. The pure substance melted at 259.5° to 260.5° C. and did not depress the melting point of the Friedel-Crafts' isomer-produced in the smaller proportion.

Concentrated sulphuric acid added to the 1-naphthoyl acid turns it orange immediately. The acid dissolves to form an orange solution changing to greenish blue and then to an indigo color—particularly on warming. The β -acid treated similarly gives a violet solution becoming purple on warming to 100° C. An attempt was made to ascertain the orientation of the 1-naphthoyl acid from the Friedel-Crafts' reaction by oxidation with potassium permanganate. While oxidation occurred readily only benzoic acid could be identified with certainty from the small amount of material available. A long continued attempt to reduce the 1-naphthoyl acid by Martin's modification of the Clemmensen procedure gave none of the desired reduction product. Attempted reduction by zinc dust and ammonia gave no more favorable result.

Methyl β -1-Naphthoyl- α,β -diphenylpropionate and Methyl β -2-Naphthoyl- α,β -diphenylpropionate

Both of these esters were obtained in excellent yield by the usual process of heating the appropriate acid with methanol and sulphuric acid. The methyl ester of the 1-naphthoyl acid was obtained by recrystallization from methanol

as transparent cubical crystals, m.p. 157.5° to 158.1° C. Calc. for $C_{27}H_{22}O_3$: C, 82.2; H, 5.62%. Found: C, 82.5; H, 5.48%. The methyl ester of the 2-naphthoyl acid was recrystallized from methanol, m.p. 194.4° to 194.9° C. Found: C, 82.5; H, 5.46%.

α,β -Diphenyl- β -anisoylpropionic Acid

This acid was prepared from anisole, diphenylsuccinic anhydride, and aluminum chloride in tetrachloroethane, using the same procedure as described above for the naphthoyl compounds. From 5 gm. anisole and 10 gm. of the anhydride 11.5 gm. of the crude acidic product was isolated. Recrystallization was effected from ethanol. The pure material appeared as small transparent lathlike crystals, m.p. 229° to 230° C. Calc. for $C_{23}H_{20}O_4$: C, 76.64; H, 5.59%. Found: C, 76.48; H, 5.54%. The substance on oxidation gave *p*-anisic acid, thus showing the orientation.

*α,β -Diphenyl- γ -*p*-methoxyphenylbutyric acid, $CH_3O.C_6H_4.CH_2CH(C_6H_5)CH(C_6H_5)CO_2H$*

A neutral solution of the sodium salt of β -anisoyl- α,β -diphenylpropionic acid was made from 2.6 gm. of the acid by dissolving it in dilute caustic soda and carefully neutralizing with hydrochloric acid. The solution was heated for 24 hr. at 165° C. with hydrogen at 3950 p.s.i., using the Adkin's copper chromite catalyst. The catalyst was removed and the solution acidified, giving an almost quantitative yield of the crude reduced product. This was recrystallized repeatedly from ligroin (b.p. 60° to 90° C.) when the *p*-methoxytriphenylbutyric acid was obtained, m.p. 123° C. Calc. for $C_{23}H_{22}O_3$: C, 79.75; H, 6.40%. Found: C, 79.73; 79.76; H, 6.20; 6.40%.

Diphenylsuccinic Ester and Ethyl Magnesium Iodide. Lactone of α,β -Diphenyl- γ -ethyl- γ -hydroxy Caproic Acid

On adding the Grignard reagent prepared from 2.43 gm. of magnesium turnings and 18.7 gm. ethyl iodide to a suspension of 32.6 gm. of diphenylsuccinic ester, m.p. 141° C., in anhydrous ether and refluxing and stirring for four hours no perceptible reaction was noticed and the ester was recovered unchanged. No improvement was noticed when the ester was dissolved in benzene. Again, using the same equimolecular proportions of the reactants but placing the ester in a Soxhlet apparatus no action occurred.

In a further trial an excess of Grignard was used, namely, 0.25 mole of Grignard reagent from 6.07 gm. magnesium to 0.05 mole of diphenylsuccinic ester (16.3 gm.). Refluxing was continued for 12 hr. After the reaction mixture had been decomposed with 5% sulphuric acid the ethereal layer gave a viscous oil on evaporation of the ether. Trituration of this oil with alcohol caused crystalline material to separate which ultimately gave 2.5 gm. of colorless needles, m.p. 156.6° C. Calc. for $C_{26}H_{22}O_2$: C, 81.60; H, 7.53%. Found: C, 81.78; 82.02; H, 7.58; 7.72%. The substance dissolves in hot

sodium hydroxide but not in sodium bicarbonate; hence it acts as a lactone rather than as a ketone.

Diphenyldibenzoylthane (Bidesyl) from Diphenylsuccinyl Chloride

Diphenylsuccinyl chloride (10), 8 gm., was suspended in 150 ml. thiophene-free benzene and 10.5 gm. aluminum chloride added with stirring. After the reaction mixture had stood overnight the mixture was treated with ice and hydrochloric acid and the benzene removed by steam distillation. The crude product (9 gm.) was gummy but hardened later when it was recrystallized from butyl cellosolve, m.p. 260° C. Its melting point and color reaction with sulphuric acid agreed with former descriptions of the high melting form of bidesyl, and its identity was confirmed further by analysis. Calc. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68%. Found: C, 86.08; H, 5.90%.

Acknowledgments

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